

# REPORT DOCUMENTATION PAGE

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6. AUTHOR(S) Dr. Rodney J. Bartlett		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Quantum Theory Project University of Florida PO Box 118435 Gainesville FL 32611-8435		8. PERFORMING ORGANIZATION REPORT NUMBER
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## 13. ABSTRACT (Maximum 200 Words)

We have emphasized a rational theoretical design of new energetic metastable molecules that is based on highly accurate electron-correlated coupled-cluster theory and directed toward a search of "synthesizable" species that have a high heat of formation (large specific impulse) and can be reasonably stable. We have investigated the molecular mechanisms of the initial steps in exothermic decomposition (initial steps of ignition and explosion), as well as possible synthetic roots in the synthesis of the desired metastable isomers. Based on the goal of developing theoretical methods that can provide sufficiently high accuracy (to be competitive with what experimental methods can achieve for the characterization of molecular structure and properties), we have formulated and implemented in the ACES II program the following new "tools": ROHF-CC and ROHF-MBPT methods for the treatment of open-shell systems that might be subject to spin contamination in UHF; analytical gradients for ROHF-CC and ROHF-MBPT; the equation-of-motion coupled-cluster (EOM-CC) approach for excited, electron-attached, and ionized states; triple excitations for excited-state energies; simplified (partitioned) EOM-CC methods for application to large molecules; and EOM-CC method for computations of properties, including NMR coupling constants.

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# REPORT OF INVENTIONS AND SUBCONTRACTS

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University of Florida  
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## SECTION I - SUBJECT INVENTIONS

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**a. NAME(S) OF INVENTOR(S)  
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**b. TITLE OF INVENTION(S)**

**c. DISCLOSURE NO.,  
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SERIAL NO. OR  
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**AIR FORCE OFFICE OF SCIENTIFIC RESEARCH**

**FINAL REPORT AFOSR F49620-95-1-0130**

**2/1/95-1/31/98**

**METASTABLE MOLECULES AND OTHER ENERGETIC STRUCTURES:  
THE CONTRIBUTION OF THEORY**

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QUANTUM THEORY PROJECT  
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## I. INTRODUCTION

Our prior work for AFOSR has focused on developing electron-correlated *ab initio* theory, implementing new computational methods, and predicting new, high-energy molecules. Our recent (last three years) achievements in this field are summarized in the published papers and conference presentations listed in Sections IV and V. We have emphasized a rational theoretical design of new energetic metastable molecules that is based on highly accurate electron-correlated coupled-cluster theory and directed toward a search of "synthesizable" species that have a high heat of formation (large specific impulse) and can be reasonably stable.

We have investigated the molecular mechanisms of the initial steps in exothermic decomposition (initial steps of ignition and explosion), as well as possible synthetic roots in the synthesis of the desired metastable isomers. The barriers and the transition structures of these reactions provide clear clues to possible synthetic approaches and to the stability of all final and intermediate species, as well as provide the spectroscopic "fingerprints" in assessing the pathways the actual reactions will follow.

Based on the goal of developing theoretical methods that can provide sufficiently high accuracy to be competitive with what experimental methods can achieve for the characterization of molecular structure and properties, in this work we have formulated and implemented in the ACES II program the following new "tools":

- ◆ ROHF-CC and ROHF-MBPT methods for the treatment of open-shell systems that might be subject to spin contamination in UHF
- ◆ Analytical gradients for ROHF-CC and ROHF-MBPT
- ◆ The equation-of-motion coupled-cluster (EOM-CC) approach for excited, electron-attached, and ionized states
- ◆ Triple excitations for excited-state energies

- ◆ Simplified (partitioned) EOM-CC methods for application to large molecules
- ◆ EOM-CC method for computations of properties, including NMR coupling constants

The synthesis of new high-energy density materials, rocket propellants, and explosives has reached a limit where the design of a new HEDM will require a detailed knowledge of molecular mechanisms and eventually of rate constants of reactions that lead to the formation or to the decomposition of metastable molecules. In general, the increase in energy content (heat of formation) would rather decrease the stability of the substances, if there are no particular electronic mechanisms (e.g., aromatic stabilization or other delocalization effects arising from symmetry) or geometrical factors (e.g., separation of reactive groups by bulky substituents or by solvent molecules), which stabilize the energetic molecules. Nevertheless, one should remember that approaching the limit of chemical energy storage will also decrease the effect of electronic stabilization. This pertains not only to the final energetic molecules, but also to the reaction intermediates, which may cause the decomposition of the final product at the moment of its formation. Thus only a detailed knowledge of the reaction mechanisms can help to synthesize and to find the requisite conditions to prevent immediate decomposition of very energetic species.

## **II. SUMMARY OF PRINCIPAL RESULTS**

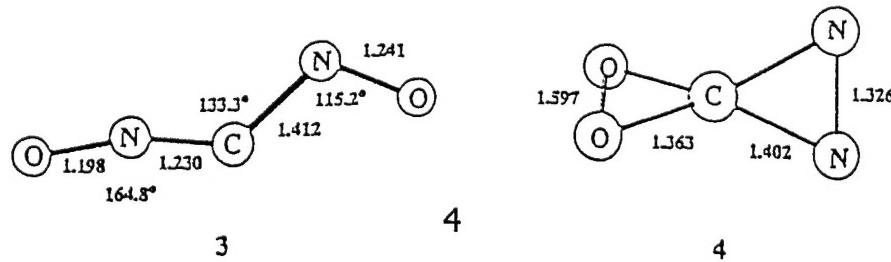
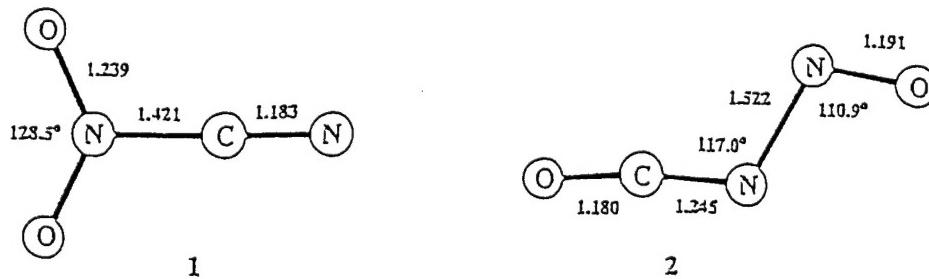
*Ab initio* computations of the heats of formations and structures of known or easily predicted unknown molecules have become routine using programs like ACES II, Gaussian or GAMESS. ACES is a user-friendly program which allows it to be employed as a tool by an experimental chemist without requiring a special knowledge of theory, yet it incorporates the newest developments we are making in CC/MBPT and their excited-state extensions. This has enabled us to make comprehensive studies of new energetic molecules including possible synthetic routes and decomposition reactions. Besides incorporating our new

methods, we are also trying to improve the performance of the ACES II program with the intention of providing it as an easily used universal tool for structural, energetic, and spectroscopic studies of metastable molecules.

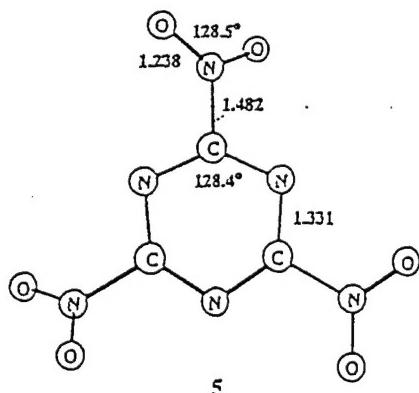
### A. New, Potential Monopropellants and Oxidizers

One of our objectives has been to pursue systematic studies of small energetic molecules that exhaust the isomeric possibilities. In this way, we have explored the  $\text{CN}_2\text{O}_2$  [25] and  $\text{CN}_2\text{O}_3$  [31] systems, while also considering selective dimers and trimers [26].

**1.** Nitryl cyanide,  $\text{NC-NO}_2$  {1} [25] is composed of two energetic groups, CN and  $\text{NO}_2$ . The estimated large values of the heat of formation ( $\Delta H_f^0 = 60 \text{ kcal/mol}$ ) and of the decomposition energy of **1** (**1**  $\rightarrow \text{N}_2 + \text{CO}_2$ ;  $\Delta E = 150 \text{ kcal/mol}$ ) make this species potentially interesting as a high-energy molecule. Nitryl cyanide can be a reasonably stable molecule as its C-N bond dissociation energy (59 kcal/mol) and the barrier to decomposition into  $\text{N}_2$  and  $\text{CO}_2$  (54 kcal/mol) are rather high, being comparable to nitromethane. Nitrosoisocyanate,  $\text{ONNCO}$  {2}, earlier studied as a collision complex in the reaction of NCO and NO (M.C. Lin and C. F. Melius, J. Phys. Chem. 1993, 97, 9124) is the most energetically favorable  $\text{CN}_2\text{O}_2$  isomer, but its 18 kcal/mol unimolecular dissociation barrier is very low. Thus **2** can only be observed as a short-lived intermediate. Nitrosoulnimate,  $\text{ONCNO}$  {3}, and its bicyclic isomer {4} are even more energetic than **1**, but they are apparently less stable.



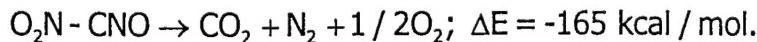
**2.** 2,4,6-trinitro-1,3,5-triazine (TNTA) {**5**} [26] is the cyclic trimer of **1**. The formation of molecular complexes (e.g., di-, tri-, oligo-, and polymers) is a conceivable way to increase density and stability and to improve the material properties of propellants and explosives. Trinitrotriazine has an intriguing history. As suggested in 1907 (Finger, H., J. Prakt. Chem. 75, 103 [1907]), one might expect the synthesis of TNTA from industrially available cyanuric chloride (2,4,6-trichlorotriazine) and AgNO<sub>2</sub>, however, this does not occur. All previous efforts to synthesize **1** failed, and no further information about preparation or characterization of TNTA is available in the literature. Our computational results show that TNTA can be reasonably stable, if the proper synthetic route is found.



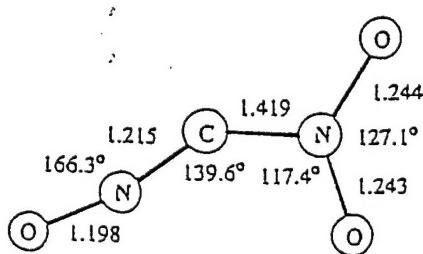
The minimum energy C3 structure of TNTA computed at the MBPT(2)/6-31G\* level has a planar aromatic six-membered ring with the NO<sub>2</sub> group rotated out of the ring plane by 40°. The out-of-plane rotation of NO<sub>2</sub> groups compromises the conjugation of the nitro groups and the aromatic six-electron ring system (maximum for the planar form) and repulsion of negatively charged oxygens and ring nitrogens (minimum for the 90° rotation). The 46 kcal/mol heat of formation of TNTA can be obtained from an isodesmic reaction, and the estimated heat of formation of TNTA in the solid state is 24 kcal/mol lower than its gas phase value. Once we have an estimate of ΔH°<sub>f</sub> for TNTA, its 304 kcal/mol energy release in decomposition into N<sub>2</sub> and CO<sub>2</sub> (ΔE<sub>r</sub>), specific decomposition energy (1410 cal/g; ΔE<sub>r</sub> divided by the molecular mass) and

specific impulse (269 s in the atmosphere and 294 s in the vacuum) can be easily derived. Our estimates of  $\Delta E_r$  and  $I_{sp}$  for TNTA demonstrate its performance to be similar to that of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), but the estimated density of TNTA ( $2.1 \text{ g/cm}^3$ ) is higher than in RDX ( $1.82 \text{ g/cm}^3$ ).

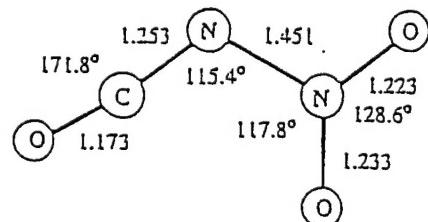
**3.** Nitrofulminate, ONC-NO<sub>2</sub> {6} [31], N-oxide of nitryl cyanide, promises to be a very powerful oxidizer, if a method for its synthesis is found. Regarding its high exothermicity in decomposition, nitrofulminate is suggested as a potential energetic oxidizer. The estimated gaseous heat of formation of nitrofulminate is 71 kcal/mol, and it has very high exothermicity in decomposition:



Another CN<sub>2</sub>O<sub>3</sub> isomer, nitroisocyanate, OCN-NO<sub>2</sub> {7} is a collision complex in the gas phase reaction of NO<sub>2</sub> and NCO radical. The reaction of NO and NCO has a similar mechanism that involves the formation of the unstable nitrosoisocyanate, OCN-NO. Among other reasons, an interest in the experimental and theoretical studies of reactions of NCO with NO<sub>x</sub> occurs because of their importance for the process of effective removal of No<sub>x</sub> from exhaust gases—the rapid reduction of nitrogen oxide (RAPRENO<sub>x</sub>) (Perry, R. A., Siebers, D. L., Nature 324, 657 [1986]).



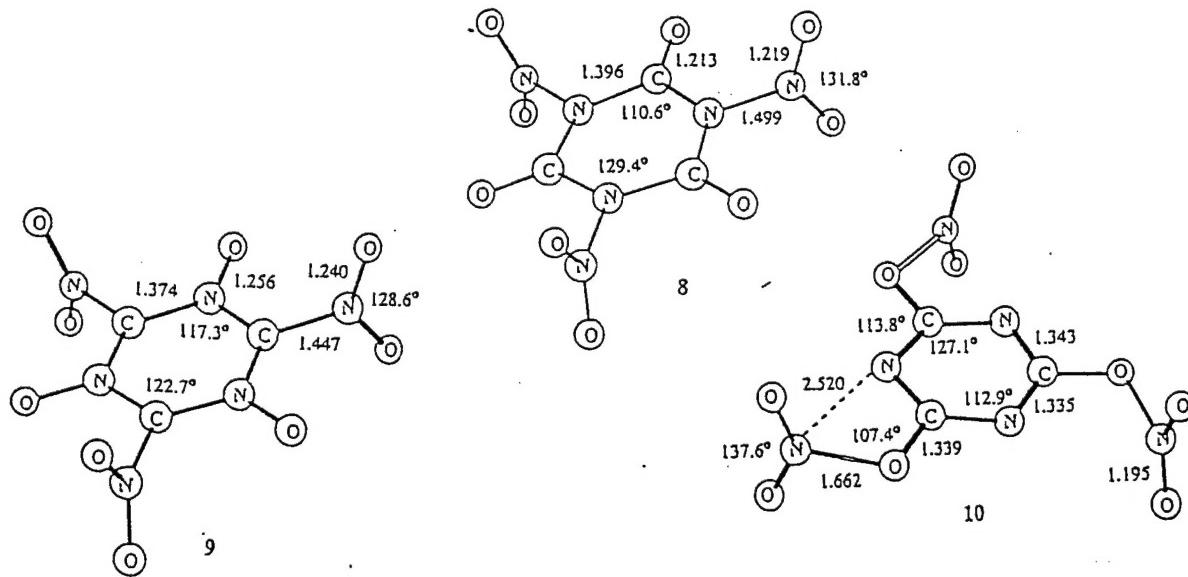
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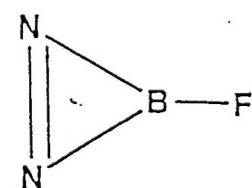
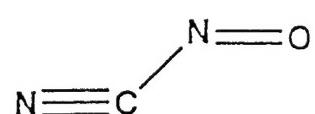
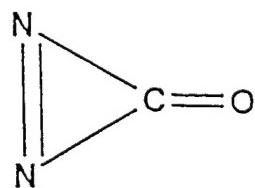
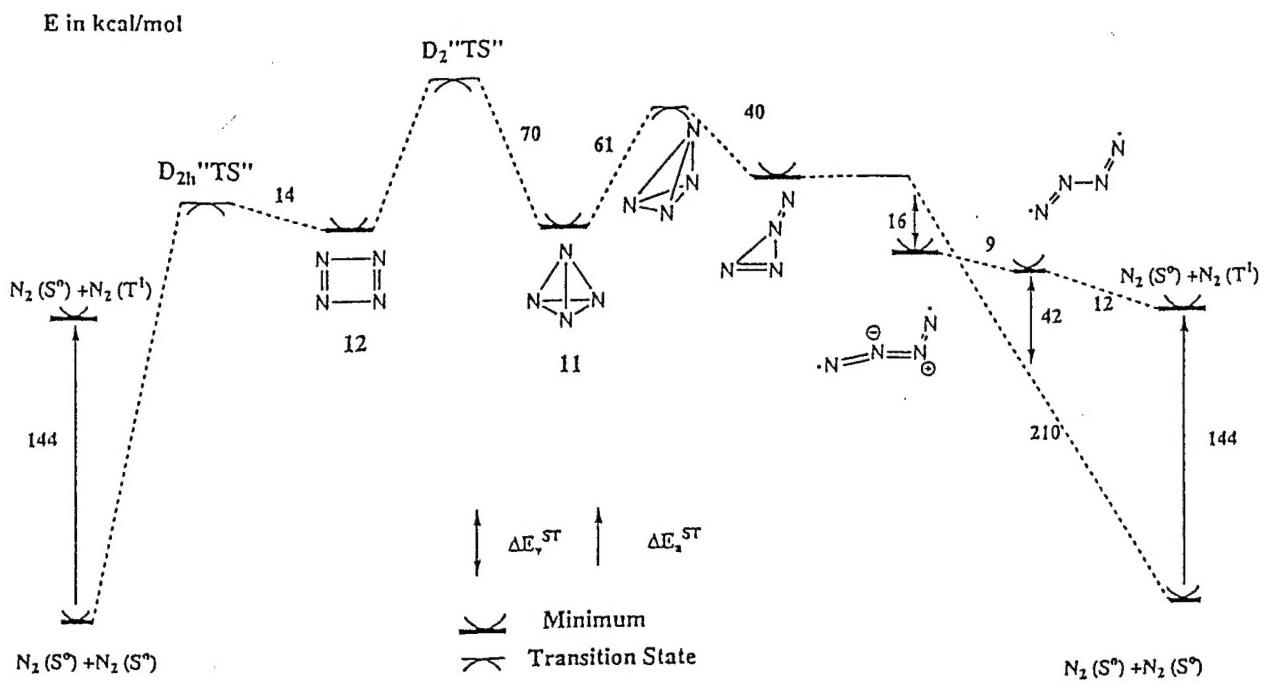
**4.** Trinitrotriazine trioxide (TNTATO) {8} [31] is an analog of triazine, but the increased number of oxygen atoms offers **7** as a potential oxidizer with a high heat of formation ( $\Delta H_f(g) = 108 \text{ kcal/mol}$ ). As estimated in composite

liquid and solid propellants, the performance of TNTATO is comparable to that of the most energetic, experimentally known oxidizers. The formation of two other cyclic triazine-type,  $(\text{CN}_2\text{O}_3)_3$  trimers **{9, 10}** which have lower energy, may complicate the synthesis of **8** or decrease its stability.

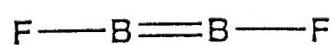


**5.** The 20, eight-electron-four-atom metastable molecules represent another type of grouping that might be explored to assess some characteristics of energetic species. This was suggested as an extension of our previous research on the nitrogen dimer [21]. We have found that the alternative decomposition pathway of tetraazatetrahedrane **{11}** via the planar four-membered anti-aromatic tetrazacyclobutadiene **{12}** has a higher barrier than the direct decomposition into two  $\text{N}_2$  molecules.

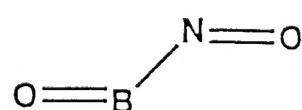
A few other molecules of the series have interesting structural, energetic, and spectroscopic features that can be of potential interest for further experimental study and possible applications. Thus two  $\text{CN}_2\text{O}$  isomers, diazirinone **{13}** and nitrosyl cyanide **{14}**, are high-energy molecules. Although 14 has a somewhat higher energy, it is known experimentally; 13 is unknown. Other unknown molecules with intriguing properties are fluorodiazaboririne **{15}**, ethylenedione **{16}**, difluorodiborene **{17}**, and nitrosoboroxide **{18}**.



16



17



## B. Methodological Advances

We have made substantial progress in the following areas:

- ◆ Investigation of the equation-of-motion coupled-cluster approach for excited, electron-attached, and ionized states;
- ◆ Introduction and assessment of the effects of triple excitations on excitation energies;
- ◆ Study of simplified (partitioned) EOM-CC methods for application to large molecules;
- ◆ Consideration of the application of EOM-CC to properties, including NMR coupling constants.

**1.** The electronic excitation (EE) EOM-CC limited to single and double excitations (i.e., EOM-CCSD) has now been applied to a range of difficult systems, including the molecules Cl-O-Cl [14], formaldehyde, acetylaldehyde, and acetone [12], the polyenes (ethylene, butadiene, cyclopentadiene) [24], and benzene and the azabenzenes [30]. It is clear from these studies that with well polarized and diffuse basis sets, EE-EOM-CCSD is accurate to within about 0.3 eV, except in cases where the excited state is dominated by a double excitation. Whereas the errors are small for Rydberg states, they tend to also be large for some valence excited states. The above points to a need for triple excitations to rectify the problem with doubly excited states and with certain valence states.

**2.** A hierarchy of triple-excitation-corrected EOM-CC methods has been introduced in the last two years of this project [9, 23]. There are iterative approximations based on our CCSDT-1 [Y. S. Lee and R. J. Bartlett, *J. Chem. Phys.* 134, 126 (1984)] and CCSDT-3 [J. Noga, R. J. Bartlett, and M. Urban, *Chem. Phys. Lett.* 134, 126 (1987)] methods, as well as their corresponding non-iterative approximations, EOM-CCSD(T) [9] and EOM-CCSD( $\tilde{T}$ ) [23]. The non-iterative methods depend on two and three  $n^3N^4$  steps, respectively, rather than  $n^3N^4 \times N_{it}$  as in the iterative methods, so they can be applied to larger molecules. The EOM-CCSDT-1 and (T) methods have been shown to offer much improved

results for double excited states, while they do little for the valence excited states. However, the EOM-CCSDT-3 offers substantial improvement for both, showing exceptional agreement in comparisons to the full CI limit for several small molecules [23]. Most of this accuracy is retained by the much less expensive EOM-CCSD(T). For the polyenes [24] and azabenzenes [30], the average error for the latter, compared to experimentally established, vertical excitation energies, is about 1.0 eV. It does overestimate the triple correction compared to EOM-CCSDT-3 for some difficult cases, however.

**3.** For large-scale applications even EOM-CCSD is highly demanding, as nonsymmetric matrices of rank exceeding  $10^6$  must be partially diagonalized iteratively, to extract the eigenvectors and eigenvalues. Consequently, we have investigated approximations based upon partitioning such large matrices to greatly reduce the computational complexity while retaining most of the accuracy of the full EOM-CCSD. In particular, we introduced the p-EOM-CCSD and its second-order perturbation theory analogue, p-EOM-MBPT(2) [17]. The latter requires only an  $n^2N^3$  algorithm compared to  $n^2N^4$  for the EOM-CCSD, and serves as the analogue of the highly successful MBPT(2) treatment for ground states. In applications to ethylene, butadiene, formaldehyde, and acetylaldehyde, the p-EOM-MBPT(2) method shows an average error of 0.12eV compared to the full EOM-CCSD results. However, for significantly large systems, such a calculation is one to two orders of magnitude faster while also being far less demanding of computer resources.

**4.** The electron-attached (EA) EOM-CC was formulated and implemented recently [10]. Besides the obvious application to electron affinities, it is ideally suited to describing systems that differ by one electron from a closed shell. An example is offered by our work on the Li embedded cryogenic cluster problem. For such a system (consisting of an alkali metal atom, M, plus a closed shell species— $H_2$ ,  $N_2$ , He, Ne, Ar, etc.), we can study the excited states by first performing CC calculations on the  $M^+ + H_2$  system and then using EA-EOM-CC to systematically add an electron into each of the unoccupied orbitals in the cation.

This conceptually appealing route also has numerical advantages, as there are fewer coefficients to determine than in EE-EOM-CC, yet it provides a direct, fully correlated calculation of the comparatively small energy difference. Such an approach benefits from the large similarity between the correlation problem for the cation and the neutral molecule. For the Li + H<sub>2</sub> system, our answers are exceptional, although the simultaneous description of the weak ground state Van-der-Waals interaction, in addition to that for the excited states, makes the problem exceedingly difficult. The EA-EOM problem is also pertinent to our newly proposed STEOM-CC.

**5.** A very convenient treatment of second-order properties is a byproduct of the EOM-CC approach. Those of primary interest here are the spin-spin coupling constants since, unlike NMR chemical shifts, they have not been adequately described in prior theory. Furthermore, they offer characteristic values that can identify various bonding situations likely to be encountered in atom-doped cryogenic solids. To enable theory to handle this problem, we introduced new EOM-CC property methods [3, 4] in 1994. This work demonstrates that it is necessary to include all four of the contributions to the coupling constant (i.e., the Fermi contact), spin-dipolar, paramagnetic spin orbit, and the diamagnetic terms, if predictive accuracy is to be attained. Good basis sets and high (CC) levels of electron correlation are required. After calibration [19], where we determined average errors of 4 Hz (or less than about 10% for the coupling constants), we had a tool to make "predictive" applications. We did so for the fascinating carbocations, which can assume non-classical structures. First we studied the ethyl carbenium ion [13]. This prototypical primary alkyl cation has never been observed experimentally, but our calculations provide a coupling constant of  $13 \pm 7$  Hz for the bridged H-C, which would serve as a fingerprint for the non-classical H, as the usual H-C constant is about 120 Hz. Similarly, the bridged C to a normal C coupling constants in the 2-norbornyl cation (the system studied extensively by G. Olah) have never been determined experimentally. Our calculation [22], which provides excellent agreement with

the constants that were determined, predicts -5 Hz compared to the normal C-C constants, which are about +33 Hz.

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### **III. PERSONNEL SUPPORTED**

#### **Graduate Students**

- (1) Dr. Steve Gwaltney (PhD 1997)
- (2) Dr. Ajith Perera (PhD 1996)
- (3) Mr. Piotr Rozyczko (PhD expected 1998)
- (4) Mr. Anthony Yau (AASERT grant)

#### **Other personnel**

- (1) Dr. Anna Balkova
- (2) Dr. Anatoli Korkin
- (3) Dr. Marcel Nooijen
- (4) Dr. Renee Peloquin Mattie
- (5) Mr. Sullivan Beck

### **IV. PUBLICATIONS SUPPORTED BY F49620-95-1-0130**

1. S.R. Gwaltney and R. J. Bartlett "An application of the equation-of-motion coupled cluster method to the excited states of formaldehyde, acetaldehyde, and acetone," *Chem. Phys. Lett.* **241**, 26-32 (1995).
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## V. INVITED PRESENTATIONS

- (1) September 1997—"The equation-of-motion coupled-cluster method and its similarity-transformed (STEOM) variant as a unified treatment of excited, ionized, electron-attached states and properties," International Conference on "Electron Correlation: From Atoms to Biomolecules." Glumslöv, Sweden.
- (2) June 1997—"The interface between DFT and *ab initio* correlated methods," Symposium on Density Functional Theory and Applications." Duke University, Durham, North Carolina.
- (3) February 1997—"Non-linear optical properties of molecules: The role of quantum chemistry," Wright Patterson Air Force Base, Dayton, Ohio.
- (4) February 1997—"Electron correlation in extended systems: The next frontier?" Ohio Supercomputer Center, Columbus, Ohio.

- (5) October 1996—"Electron correlation in polymers," Swedish-American Symposium on the Foundations of Quantum Theory in Chemistry, Molecular Physics and Biology: A Symposium in Honor of Per Olov Löwdin." Sanibel Island, Florida.
- (6) August 1996—Battelle Northwest Laboratories, EMSL Theory, Modeling and Simulation Workshop, "Recent Developments in Coupled-Cluster Theory Implemented into the ACES II Program System." Richland, Washington.
- (7) July 1996—"The First Principle Prediction of Coupling Constants for Carbocations and Other Molecules," World Association of Theoretically Oriented Chemists (WATOC) Congress, Jerusalem, Israel.
- (8) June 1996—"Extended States for Molecules and Clusters," HEDM Meething, Boulder, CO, 1996.
- (9) April 1996—"NMR Coupling Constants with the Equation-of-Motion Coupled-Cluster Method," 2<sup>nd</sup> International Congress on Theoretical Chemical Physics, New Orleans, LA.
- (10) March 1996—"Perturbation Approaches for Excited States," Research Symposium on Multiconfigurational Perturbation Theory: Methods and Applications. Gandia, Spain.
- (11) December 1995—"Challenges for HPCC," Computational Chemistry Focus Group, Maui, Hawaii.
- (12) November 1995—"Electronic Excited States of Organic Molecules," Joint Regional ACS Meeting, Memphis, TN
- (13) October 1995—"Carbon Cluster C<sub>2</sub>–C<sub>10</sub>: The Synergism between Theory and Experiment," Korean Advanced Institute of Science and Technology, Taejon, Korea.
- (14) October 1995—"An Introduction to Coupled-Cluster Methods and Other Correlated Approaches," Postec University, Pohang, Korea.
- (15) October 1995—"Coupled-Cluster Theory as a Unified Approach to Molecular Spectroscopy: Vibrational, Electronic, and NMR," Korean Chemical Society, Pusan, Korea.
- (16) September 1995—"Equation-of-Motion Coupled-Cluster Method for Excited, Ionized, and Electron-Attached States," Molecular Quantum Mechanics: Methods and Applications Conference, University of Cambridge, Cambridge, England.
- (17) August 1995—"Excited States Using the Equation-of-Motion Coupled-Cluster Method," 12<sup>th</sup> Canadian Symposium on Theoretical Chemistry, University of New Brunswick, Fredericton, Canada.
- (18) June 1995—"Analogues of Tetrahedral N<sub>4</sub> as Potential High-Energy Molecules," Air Force High Density Materials Contractors' Conference, Woods Hole, MA.

- (19) May 1995—"Equation-of-Motion Coupled-Cluster Methods for Excited, Ionized, and Electron-Attached States," Pople Symposium, Northwestern University, Evanston, IL.
- (20) May 1995—"Equation-of-Motion Coupled-Cluster Methods with Application to  $\text{BCl}_3$ ," Air Force Office of Scientific Research Contractors' Meeting, Wright-Patterson Air Force Base, CA.
- (21) January 1995—Air Force Office of Scientific Research HEDM Theory-Synthesis Workshop, Palmdale, CA.

#### **University Colloquia Presented**

February 1997—Tulane University, New Orleans, Louisiana  
December 1996—University of Torino, Torino, Italy  
April 1996—University of North Texas, Denton, TX  
April 1996—Southern Methodist University, Dallas, TX  
April 1996—University of Texas at Arlington, Arlington, TX  
October 1995—Lehigh University, Bethlehem, PA  
March 1995—Iowa State University, Ames, IA

#### **V. HONORS, AWARDS**

##### **David L. Williams Term Professorship**

Dr. Rodney J. Bartlett has been designated the 1997-1998 David L. Williams Term Professor in the College of Liberal Arts and Sciences at the University of Florida. The award is given in recognition of outstanding scholarship and teaching and carries with it a one-year supplement of \$5,000 in salary and \$1,000 in research support.

##### **University of Florida Research Foundation Professorship Award**

Dr. Rodney J. Bartlett has been awarded a 1998 University of Florida Research Foundation Professorship. These are three-year professorships to recognize faculty who have distinguished records of research and scholarship that clearly will be sustained. The award includes a salary bonus and research support money.